وزارة الزراعة واستصلاح الأراضي
Ministry of Agriculture and Land Reclamation
مركز البحوث الزراعية
Agricultural Research Center

Egyptian Journal of Plant Protection Research Institute

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PLANT PROTECTION RESEARCH INSTITUTE PPRI

Green silver nanoparticles production by and against the two-spotted spider mite *Tetranychus urticae* (Acari: Tetranychidae)

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ARTICLE INFO
Article History
Received: 16 / 1 / 2020
Accepted: 26 / 3 /2020

Keywords
Tetranychus, biosynthesized, AgNPs, biogenic amines, reactive oxygen scavengers and sterility.

Abstract:

The novel method to produce green silver nanoparticles by *Tetranychus urticae* Koch. (Acari: Tetranychidae) was depicted to provide new biocides. It was started by the exposure of adult females of *T. urticae* to little amounts of silver nitrate AgNO3.Then, table-salt, sodium chloride, was used as an intermediate compound to produce biological spherical silver nanoparticles (AgNPs) by mites. Coating with biogenic amines released from exploded *T.urticae* was detected by monoamine oxidase interaction. Then, such a structure played an important role to penetrate the integument of exposed *T.urticae* easily. Bio-nanoparticles of silver produced from the green form of *T.urticae*, which caused certain mortality percentages over 97% against the same species, while they were more than 90% against the red form of *T.urticae*. In the same trend, the bio product from the red form of *T.urticae*, caused mortality over 88% and 94% in the case of treatments against green and red *T.urticae* forms, respectively. Consequently, determined LC50s of bio AgNPs from green against both forms were 20.58 and 31.81 μLL^{-1} while they were 29.24 and 58.35 μLL^{-1} of bio AgNPs from red *T.urticae* and against the same arrangement of morphs. Therefore, AgNPs resulted from the green form of *T.urticae*, caused sterility with 91.21% and 86.07 % in case of treatments against *T.urticae* green and red forms, respectively. Also, AgNPs from the red form of *T.urticae*, caused sterility with 88.68% and 94.21 % in case of treatments against the same arrangement of morphs, in comparison with control. Revealed data showed that oxidative stress interacted effectively by increase with induced treatments. Reactive oxygen scavengers (ROS) were significantly lower than control ($P < 0.05$). To conclude, the new trend to produce bio AgNPs by mite against the same pest presented a cheap, simple and ecofriendly method to expand the use of nanoparticles in the plant protection field.

Introduction

Pesticides are exceedingly dynamic substances that can debilitate the upholding territorial integrity of certain environments. Because of across the board pesticides to croplands, they have constituted an intemperate danger to all components of biodiversity. So the production of bio nanoparticles through unusual resources would provide a new solution to such dangerous problems. Overall, nanoparticles have advantages as pesticides which presented an evolutionary paradigm. The system of nanoparticle conveyance permits numerous naturally dynamic operators to achieve the coveted site of activity. The upsides of nanotechnology are as per the following: (I) expanded bioavailability (fast disintegration; enhanced entrance/saturation through layers); (ii) minimized required concentrations; (iii) minimized dose-dependent toxicity; (iv) monitored emission; (v) directed bio-distribution; (vi) decrease of the environmental impact on bioavailability inconstancy (Bhushan, 2004; Rao *et al*.,2005; Cheng *et al*., 2015 and Rai *et al*.,2015).

The development, solidness, and movement of nanoparticles depend not just on their shape and size-controlled dissemination at the same time, additionally on their blend root. Numerous procedures and strategies have been embraced for getting ready metallic nanoparticles of different sorts, including polyol techniques (Kim *et al*., 2007), borohydride decrease, dissolvable extraction–reduction (Esumi *et al*.,1991), sonochemical techniques (Mizukoshi *et al*.,1997), photolytic reduction, radiolytic reduction, laser removal, and micro emulsion. Besides, green synthesis of metallic nanoparticles by natural products as reducing and capping agents is represented the easiest methods, ecofriendly, and most effective techniques (Shankar *et al*.,2004; Mondal *et al*.,2011 and Mittal *et al*.,2013). Even the green process could be done in one step by biogenic reduction of the metal ion by plant extracts to get Ag and Au nanoparticles (Mittal *et al*.,2013).

So this paper provided a trial to produce AgNPs from pest against pest and coated them by biogenic amines from exploded resource production. *Tetranychus urticae* was being the resource and the required pest to control at the same time. Thereafter, toxicity and sterility of resulted bio AgNPs from both morphs of *T.urticae*, green and red, were tested against them and almost its mode of action was examined upon oxidative stress.

Materials and methods

1.Maintenance of *Tetranychus urticae* colonies:

The two forms, green and red of *Tetranychus urticae* were gathered from normally cowpea (*Vigna unguiculata*) and strawberry (*Fragaria ananassa*) plants, independently. At that point, maintenance was done on the castor bean leaf discs under laboratory conditions as indicated by Abd El-Wahab (2010) for a half year before treatments.

2. Formation of silk balls:

At that point, single discs of castor bean plants were put separately in cages (30×30×20 cm) under institutionalized conditions (26°C, 33% RH). 500 adult females of each morph were collected by fine brush and permitted to develop on each disc. The pinnacle of the wooden stick (5 cm high, 3 mm diameter) and a square piece of graph paper (2×2 mm) were fixed on the stick to scale the surface of the ball. was watched each hour to recognize the silk ball's arrangement at the development time. The ball was shaped by 500 mites for all time amassed over the wooden stick which buried in almost 2cm thickness layer of salt. When the first mites landed on the stick, the number of others moving to the highest point of the stick was tallied over a time of 10 minutes, two times a day (at 8h15 and 14h) until the expulsion of the ball at about day 18. Silk ball formed and then harvested occurred at 14 h (TH). To gather the ball, the wooden stick was painstakingly expelled from the plant and from there on the ball was gathered from the stick end with tweezers.

3.Biosynthesis of silver nanoparticles (AgNPs):

Biological silver nanoparticles (AgNPs) were synthesized by reaction with sodium chloride was done for the first time and provided an easier trend to do so. 0.01 mg $AgNO_3$ was spread on the admitted plants just once for by 500 adults of *T.urticae* and the exposure was for 3 hours. Then, the addition of 0.1 mg of NaCl as a stabilizer and as a reduction agent had occurred. Released AgNPs were attached with the silk fibers of *T.urticae* away of salt particles even in the outer or inner layers of fiber balls. Characterization of resulted AgNPs was done by scanning electron microscopy (SEM) as shown in images (1 and 2).

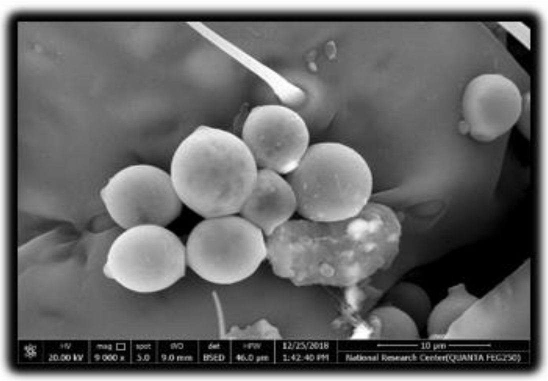

Image (1) Silver nanoparticles (100nm) coated by biogenic amines to produce full capsules

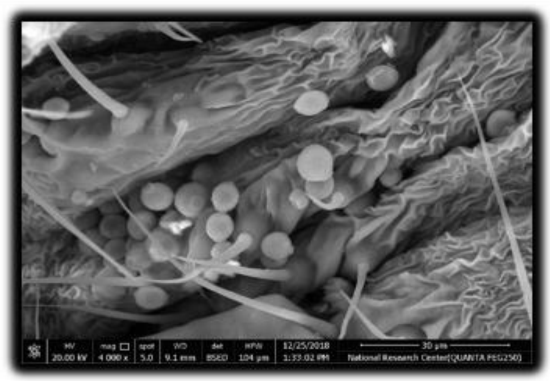

Image (2) Spherical silver nanoparticles (100nm) coated by biogenic amines from exploited bodies of *T.urticae*

4.Monoamine oxidase (MAO-A) Interaction to detect coated biogenic amines:

MAO-A is a flavin adenine dinucleotide (FAD) containing enzyme which is tightly anchored to the mitochondrial outer membrane and responsible for the reaction at equation (1).

$$R{-}\overset{H_2}{C}{-}NH_2 + O_2 + H_2O \xrightarrow[\text{oxidase}]{\text{amine}} R{-}CHO + NH_3 + H_2O_2$$

Equation (1): Reaction of Biogenic Amines with Mono Amine Oxidase (MAO).

MAO-A potencies were determined in the released homogenates as coatings of AgNPs through each interaction. The rate of the MAO catalyzed oxidation of Kynuramine was measured according to Aiyegoro and Van Dyk (2011). Kynuramine is non-fluorescent until undergoing MAO-catalyzed oxidative deamination and subsequent ring closure to yield 4-

hydroxyquinoline, a fluorescent metabolite. The concentrations of the MAO-generated 4-hydroxyquinoline in the incubation mixtures were determined by comparing the fluorescence emitted by the samples to that of known amounts of authentic 4-hydroxyquinoline at excitation (310 nm) and emission (400 nm) wavelengths. All enzymatic reactions were carried out to a final volume of 500 µL in potassium phosphate buffer and contained kynuramine as substrate, MAO-A (0.0075 mg/mL) and various concentrations of the test inhibitor (treatment). The reactions were carried out for 20 min at 37°C and were terminated with the addition of 200 µL NaOH (2 N). After the addition of distilled water (1200 µL) to each reaction, the reactions were centrifuged for 10 min at 16000 × g. To determine the concentrations of the MAO generated 4-hydroxyquinoline in the reactions, the fluorescence of the supernatant at an excitation wavelength of 310 nm and an emission wavelength of 400 nm was measured (Novaroli *et al*., 2005).

5.Toxicity of biosynthesized AgNPs against the two morphs of *Tetranychus urticae:*

The main used emulsion was prepared from the certain amount 0.01 g/L. Then bioassay was done by leaf discs of castor oil plant which dipped in prepared concentrations (Dittrich, 1962). Three replicates for each treatment with 300 mites/ replicate. Mortality results were taken after 24 hours of exposure and LC50s were estimated (Finney, 1971).

6.Assessment of the sterility effect of biosynthesized AgNPs against the two morphs of *Tetranychus urticae*:

300 mated adult females, 100 individuals/replicate, were treated with LC_{50} of bio AgNPs produced from green *T.urticae* (20.58 and 31.81 μLL^{-1}) and then red morph (29.24 and 58.35 μLL^{-1},resp., based on Finney (1971) by leaf dip technique (Dittrich, 1962). Leaf-discs were placed onto the moistened cotton pad in Petri-dishes after treatments. Both positive and negative control samples which were with 300 mated adult females for each one of both morphs as replicates vis-à-vis both treatments. Treated and untreated individuals allowed to lay eggs for 24 hours according to Abd El-Wahab (2003), then adult females were removed. Eggs were left for hatching and all required biological parameters were determined to calculate sterility percentages (Toppozada *et al*.,1966).

7.Antioxidant of enzyme activities in treated mites by AgNPs:

APX activity was measured by estimating the rate of ascorbate oxidation (extinction coefficient 2.8 mM/cm). The 3 mL reaction mixture contained 50mM phosphate buffer (pH 7.0), 0.1 mM H2O2, 0.5 mM sodium ascorbate, 0.1 mM EDTA and a suitable aliquot of enzyme extract. The change in absorbance was monitored at 290 nm and enzyme activity was expressed as the unit's min/mg protein (Nakano and Asada, 1981).

8.Data analysis:

The statistical software SPSS for Windows 16.0 was used to perform T-test. Values of $p<0.05$ and $p<0.001$ were considered as statistically significant values. Gained data through perceptions were not in every case typically dispersed. As long as, both parametric and non-parametric tests were utilized in this research. Linear regression was used to define the relation between treatments and the non-linear squares was utilized in nonlinear relationships. A paired t-test was utilized to decide the distinction between endurance paces of mites inside balls.

Results and discussion

1.Detection of biogenic amines:

Mono Amine Oxidases (MAO) was used to detect the presence of biogenic amines in the coatings of AgNPs produced by green and red morphs of *T.urticae* (Figure, 1). With lower MAO activity, the more accumulation of biogenic amines specifically with the presence of AgNPs. The specific activity as shown in Figure (1) of MAO was higher in the case of both morphs released the AgNPs than control. Affected MAO activity with 2.9 and 1.5 mOD min-1 mg-1 proteins in comparison with control (5.1 and 3.7 mOD min-1 mg-1 proteins) in green and red forms of *T. urticae*, respectively. Partial correlation between biogenic amines presented in the coatings and affected by MAO recorded .624*. Paired Samples Correlations (.247) and Paired Samples Test (t=2.410) between two morphs and resulted from ratios of MAO in comparison with control showed a non-significant difference at 95% (Sig. (2-tailed) =.028) which means that the main difference depended mainly on the certain morphs. Kendall's tau_b Correlation Coefficient between Nanoparticles and MAO =.894*, Spearman's rho=.917** and Pearson Correlation=.677* were calculated to confirm results. Moreover, R=.747*, R^2=.793, Adjusted R^2=.658. ANOVA showed that F=12.74** which showed a significant relation between MAO and certain morphs released AgNPs coated with biogenic amines.

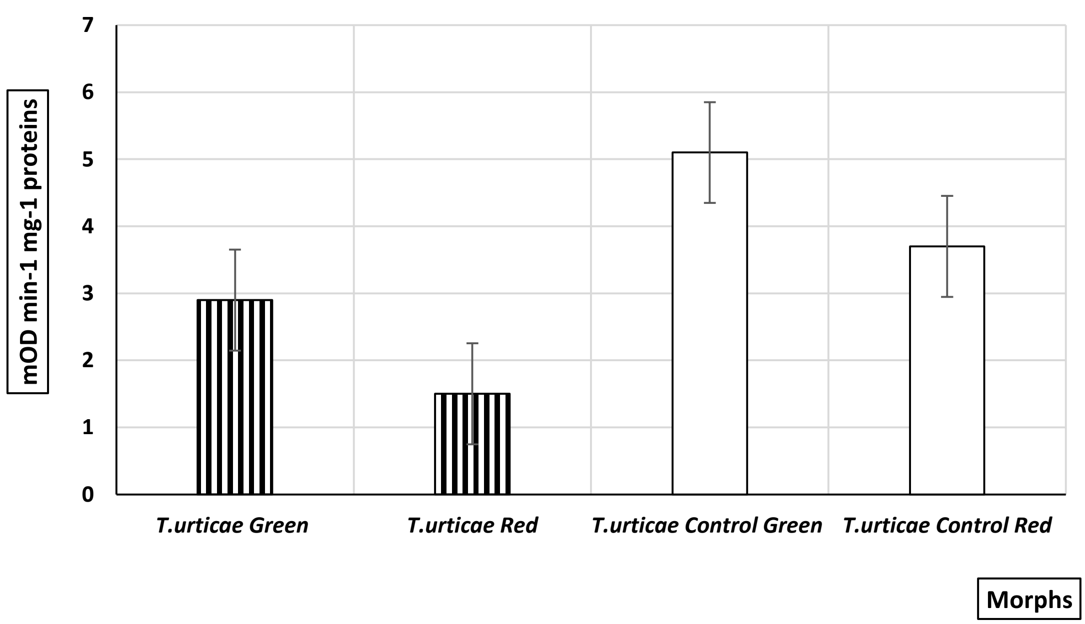

Figure (1): Monoamine oxidase (MAO) interaction to detect coated biogenic amines of AgNPs produced by certain *Tetranychus urticae* morphs .

Biogenic amines have a wide variety of functions in both the central and peripheral nervous systems of insects. They can act as neurotransmitters, neuromodulators and even circulating neurohormones. Knowledge of the pharmacology of the receptors that mediate the actions of biogenic amines in insects is increasing, there was only one known example of a pesticide that activates biogenic amine receptors. The knowledge of the mode of action of insect biogenic amine receptors is mediated through second messenger systems. Accumulation of biogenic amines played a specific role in both *T.urticae* forms and mainly red morph. Furthermore, it's proved recently that biogenic amines affected mosquito fertility. Subsequently, egg melanization was regulated by adrenergic signaling, whose disruption caused premature melanization specifically through the action of tyramine (Fuchs *et al*., 2014). Also, mosquito locomotion and survival were affected negatively by the strong cumulative of biogenic amines. Dopaminergic and serotonergic antagonists such as amitriptyline and citalopram recapitulated this effect.

Hereinafter, biogenic amines catabolism was assessed in hemolymph and saliva of *Amblyomma hebraeum* Koch. Rapidly conversion occurred of Dopamine (DA) and 5-hydroxytryptamine (5-HT) to dihydroxy phenylacetic acid (DOPAC) and 5-hydroxyindoleacetic acid (5-HIAA) respectively, indicating that monoamine oxidase (MAO) constituted a major catabolic pathway for biogenic amines in this species (Kaufman and Sloley,1996). Moreover, Deprenyl was about 44-72 times more potent an inhibitor of MAO than clorgyline when either DA or 5-HT was offered as substrate, suggesting that this MAO was of the MAOB type. Therefore, inhibition of MAO would lead to the accumulation of biogenic amines with their effects. Ceaselessly, the most widely recognized procedure is to utilize stabilizing agents that can be retained onto the AgNPs surface, maintaining a strategic distance from their agglomeration (Bai *et al*., 2007). Coating agents/surfactants could be used mainly to avoid agglomeration certainly. It can be done even by electrostatic or steric repulsion (Pillai and Kamat,2004; Oliveira *et al*.,2005 and El-Nour *et al*., 2010). Even though, any modulation of coatings, average size and distribution were affected self-assembly and stability of AgNPs (Lee and Jun, 2019).

2. Effect of Ag-Bio nanoparticles :

2.1. As miticides:

Results showed that used bio AgNPs at 0.01 g quantity which produced from the green form of *T.urticae*, caused mortality against both forms of the two-spotted spider mite, *T.urticae* in Figure (2). Mortality recorded 97.74% and 93.1% in the case of green and red forms of *T.urticae* in comparison with control (7.24 and 10.77%), respectively. Non-parametric tests were used to show the effect of the difference morphs of *T.urticae* responses to nanoparticles. Through runs test, Z =.612* was significant at 5%. Also, Wald-Wolfowitz Test was used to calculate Z for the effect of certain treatments on morphs and it was highly significant at 1% (Z=1.837**).

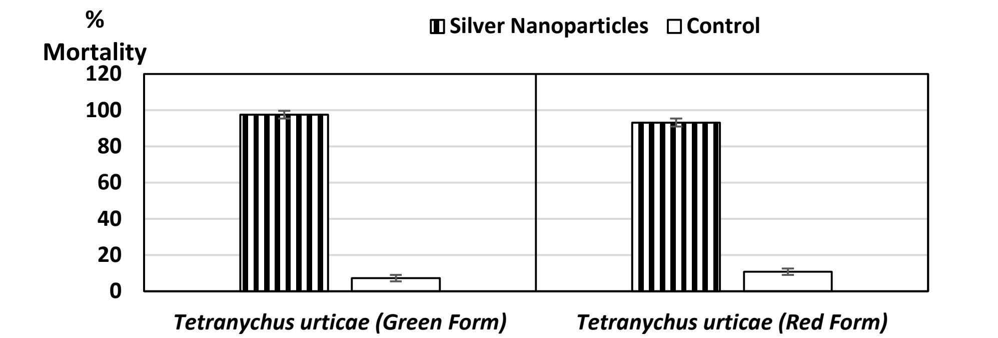

Figure (2): Effect of AgNPs from *Tetranychus urticae* (green form) against certain morphs of *T. urticae* .

Furthermore, results showed that used bio AgNPs at 0.01 g quantity which produced from the red form of *T.urticae*, caused mortality against both forms of the two-spotted spider mite, *T. urticae* in Figure (3). Mortality recorded 89.74% and 95.21% in the case of green and red forms of *T.urticae* in comparison with control (15.29 and 8.07%), respectively. Non-parametric tests were used to show the effect of the difference morphs of *T.urticae* responses to nanoparticles. Through runs test, Z =.612* was significant at 5%. Also, Wald-Wolfowitz Test was used to calculate Z for the effect of certain treatments on morphs and it was highly significant at 1% (Z=1.837**).

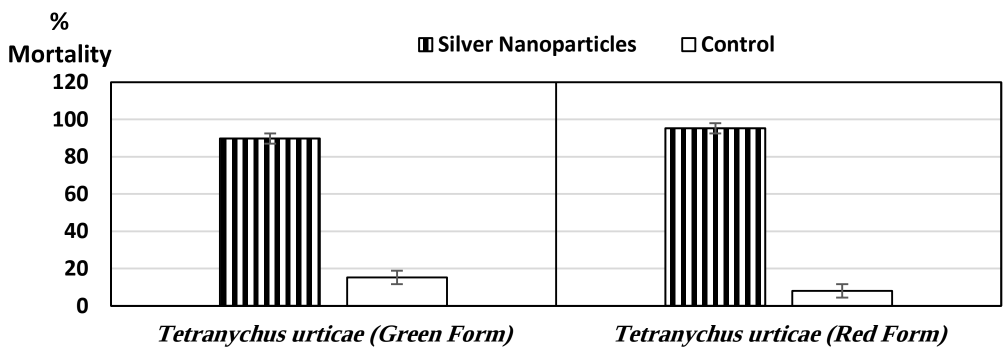

Figure (3): Effect of AgNPs from *Tetranychus urticae* (red form) against certain morphs of *T. urticae* .

2.2. As sterilants:

Produced bio AgNPs by both morphs of *T.urticae* showed a general quietly severe effect against both of them. Furthermore, results showed that used LC50s of bio AgNPs by green morph caused sterility against both forms of *T. urticae* in Figure (4) with 91.21% and 86.07% in the case of green and red forms of *T.urticae* in comparison with control (8.04 and 12.57%), respectively. Superficially, paired-samples correlations showed that between treatments, there was a highly significant difference at 1% (Std Error Mean=28868**). Kendall's Coefficient of Concordance (Kendall's W^a) = .857* and Chi-Square recorded 6.857*. Besides, Friedman Test showed a significant difference at 5% (Chi-Square=6.86*).

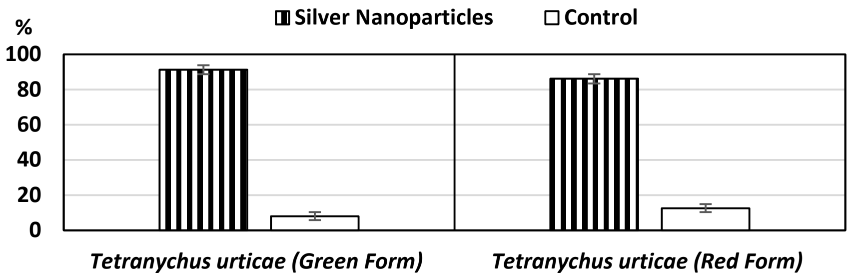

Figure (4): Sterility effect of AgNPs from *Tetranychus urticae* (green form) against certain morphs of *T. urticae* .

Consequently, results showed that used LC50s of bio AgNPs by red morph caused sterility against both forms of *T. urticae* in Figure (5) with 88.68% and 94.21% in the case of green and red forms of *T.urticae* in comparison with control (10.25 and 12.87%), respectively. Paired samples correlations showed that between treatments, there was a highly significant difference at 1% (Std Error Mean=28868**). Apparently, reliability Statistics showed Cronbach's Alpha[a]=.036 and ANOVA with Tukey's Test for Nonadditivity recorded the highest significant difference at 1% between the sterility of treatments and control (F=8014.542**) while F=4.631* at 5% for differences between both green and red morphs of *T.urticae*.

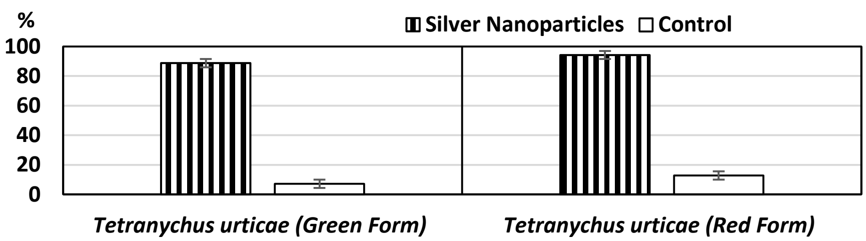

Figure (5):Sterility effect of AgNPs from *Tetranychus urticae* (red form) against certain morphs of *T. urticae* .

Nanoparticles showed repellency, acaricidal, and ovicidal effects against *Tetranychus urticae*. Acaricidal and ovicidal activities appeared clearly with nano encapsulated carvacrol and linalool, however, free compounds were more effective as repellents (Campos *et al*., 2018). Subsequently, Silver particles from cellulose/silver nanocomposites are powerful to decrease microbial development in contact with natural product exudates (Llorens *et al*., 2012). Moreover, the production of silver nanoparticles biologically by *T.urticae* was resulted to facilitate the penetration of them to other individuals after direct exposure. So problems related to physical-substance factors (e.g., ionic strength and surface charge heterogeneity) prevented either remobilization of the nanoparticles or further arrival of the active ingredient to play at any rate somewhat apart (Schweizer, 2014). Forwardly, Tetranychid mites build a typical web to ensure the settlements of their individuals. At the point when plants progress toward becoming stuffed and nourishment assets turn out to be rare, people accumulate at the plant peak to shape a ball made out of mites and their silk strings. This ball is a structure encouraging gathering dispersal by wind or creature transport (Clotuche *et al*., 2011), and the consequent dispersal of produced bio nanoparticles of silver. Furthermore, the reinforcement of more silk production is expanding the effect of AgNPs potentially.

The green nanoparticles production process offers many advantages when the comparison was being with classical chemical and physical methods since it needn't bother with the utilization of exceptionally dangerous synthetic concoctions, nor high vitality inputs (Govindarajan *et al*., 2016a, 2016b and Teimouri *et al*., 2018). The general procedure is modest, simple to do and prompts the creation of a wide exhibit of nanoparticles, including gold (Murugan *et al*., 2015a and Balalakshmi *et al*., 2017), silver (Rajakumar and Rahuman, 2012; Govindarajan and Benelli, 2016; Murugan *et al*., 2015b; Azarudeen *et al*., 2017; Aziz *et al*., 2018 and Alyahya et al., 2018), titania (Jinu *et al*., 2018), zinc oxide (Kirthi *et al*., 2011 and Ashokan *et al*., 2017), iron (Murugan *et al*., 2018), palladium (Jayaseelan *et al*., 2018) and carbon (Rajaganesh *et al*.,2016). Fundamentally, AgNPs like reduced fertility of treated insects and their movement ability was precipitously dropped (Armstrong *et al*., 2013). That was because of AgNPs ability to penetrate pest integument, and affected its life span, feeding, physiological and behavioral manifestations. Then mortality occurred (Sap-Iam *et al*., 2010), even it was detected that contact with AgNPs was more entomotoxic potential than feeding (Sedighi *et al*., 2019).

3. Reactive oxygen scavengers (ROS) :

Reactive oxygen scavengers (ROS) in treatments were significantly lower decrease than control ($P < 0.05$). Table (1) showed that Superoxide dismutase (SOD) in control was higher than treatments. Subsequently, decreased ratio percentages of SOD than control recorded 25.30 and 41.1 % by bio AgNPs at 0.01 g quantity which produced from the green form of *T.urticae* , against green and red forms, resp. In the same arrangement, but with bio AgNPs from red form, SOD ratio decreased in treatments than control with 19.1, and 26.40%.

Table (1): Reactive oxygen scavengers (ROS) ratio during Nano-metals treatments with control comparison .

Treatments	Against Green Morph		Against Red Morph	
	[1]ROS (Reactive Oxygen Scavengers) (SOD)	[2]Decreased Ratio %	[1]ROS (Reactive Oxygen Scavengers) (SOD)	[2]Decreased Ratio %
AgNPs From Tetranychus green morph	14.25±0.36a	25.30	25.07±2.71b	41.1
AgNPs From Tetranychus red morph	10.74±1.05a	19.1	16.11±1.88b	26.40
Control (green morph)	56.33c			
Control (red morph)	61.02c			

[1]ROS (Reactive Oxygen Scavengers) SOD-Superoxide dismutase (unit/mg protein).
Values are expressed as the means ±SE. Mean
[2] Decreased Ratio % = ROS ratio of the tested strain / ROS ratio of the control strain*100

Furthermore, the mode of action against insects is being through oxidative stress by a significant impact on detoxifying enzymes and antioxidants, which lead to cell death. Also, AgNPs were able to reduce the activity of acetyl-cholinesterase. Besides, Ag nanoparticles up- and downregulate key insect genes, reducing protein synthesis and gonadotrophin release, leading to developmental damages and reproductive failure. Silver nanoparticles influenced certain proteins, which are liable for neutralization of ROS, in the interacted cells. Fiery reaction and irritation are started by the gathering of reactive oxygen species (ROS), which likewise incite devastation of mitochondria and cell apoptosis (Sharma *et al*., 2015).

Crucially, silk is classified as an informative material that can provide a conspecific' turnout. It is being used as a social tool that has its impact on microhabitat, group behavior and the response of individuals (Clotuche *et al*.,2013). Three elements that could possibly impact living place decisions were controlled: the strain, number, and the phase of mites. Three factors are demonstrated their impact on the decision of microhabitat (Clotuche *et al*.,2013). The inclination of whether to settle on a silk-secured region was affected by the beginning of mites (strain impact). Grown-up females demonstrated a higher propensity to settle on a territory secured with the silk laid by various congeners (number impact). Also, hatchlings appeared to be more receptive to the nearness of silk than grown-ups (stage impact). Upon, the population of mites was able to work together to make silk balls which contained bio-AgNPs coated with biogenic amines released from exploded mites. Then prompted toxic effects of NPs have increased both chemical reactivity and penetration in cells because of small size and large surface area (Medina *et al*.,2007 and Pan *et al.*,2009). Finally, nanotechnology can alter farming and can give an answer to pest management. Bio silver nanoparticles with its properties as biocides can be a solution for even the pesticide resistance (Alif and Thangapandiyan, 2019).

References

Abd El-Wahab, R.A. (2003): Studies on some chemical compounds against some tetranychid mite species.M.Sc.Thesis., Pesticides Dept., Agric. Faculty, Mansoura Universty, Egypt.

Abd El-Wahab, R. A. (2010): Toxicity and Subtle Effects of Pesticides on Piercing Sucking Pests. pp.238. Lambert Academic Publishing GmbH & Co.KG. ISBN 978-3-8433-7596-2.

Aiyegoro, O.A. and Van Dyk, S . (2011): The antioxidant properties, cytotoxicity and monoamine oxidase inhibition abilities of the crude dichloromethane extract of *Tarchonanthus camphoratus* L. leaves. African J Biotech., 10 (75): 1729717304.

Alif, A.S., and Thangapandiyan, S. (2019): Comparative bioassay of silver nanoparticles and malathion on infestation of red flour beetle, *Tribolium castaneum*. J.Basic Appl.Zool., 80: 55. doi:10.1186/s41936-019-0124-0

Alyahya, S.A.; Govindarajan, M.; Alharbi, N.S.; Kadaikunnan, S.; Khaled, J.M.; Vaseeharan, B.; Ishwarya, R.; Yazhiniprabha, M. and Benelli, G. (2018): Swift fabrication of Ag nanostructures using a colloidal solution of *Holostemma ada-kodien* (Apocynaceae)—antibiofilm potential, insecticidal activity against mosquitoes and non-target impact on water bugs. J Photochem Photobiol B Biol., 181:70–79. https://doi.org/10.1016/j.jphotobiol.2018.02.019

Armstrong, N.; Ramamoorthy, M.; Lyon, D.; Jones, K. and Duttaroy, A. (2013): Mechanism of silver nanoparticles action on insect pigmentation reveals intervention of copper homeostasis. PLoS ONE, 8: e53186. doi: 10.1371/journal.pone.0053186.

Ashokan, A.P.; Paulpandi, M.; Dinesh, D.; Murugan, K.; Vadivalagan, C. and Benelli, G. (2017): Toxicity on dengue mosquito vectors through *Myristica frangrans*-synthesized zinc oxide nanorods, and their cytotoxic effects on liver cancer cells (HepG2). J Clust Sci, 28:205–226.

Azarudeen, R.M.S.T.; Govindarajan, M.; Amsath, A.; Muthukumaran, U. and Benelli, G. (2017): Single-step biofabrication of silver nanocrystals using Naregamia alata: a cost effective and eco-friendly control tool in the fight against malaria, Zika virus and St. Louis encephalitis mosquito vectors. J. Clust. Sci., 28(1):179–203.

Aziz, A.T.; Alshehri, A.M.; Panneerselvam, C.; Murugan, K.; Trivedi, S.; Mahyoub, J.A.; Hassan, M.M.; Maggi, F; Sut, S.; Dall'Acqua, S.; Canale, A. and Benelli, G. (2018): The desert wormwood (*Artemisia herba-alba*)—from Arabian folk medicine to a source of green and effective nanoinsecticides against mosquito vectors. J. Photochem. Photobiol. B Biol., 180:225–234.

Bai, J.; Li, Y.; Du, J.; Wang, S.; Zheng, J.; Yang, Q. and Chen, X. (2007): One-pot synthesis of polyacrylamide-gold nanocomposite. Mater. Chem. Phys., 106:412–415.doi:10.1016/j. matchemphys. 06.021.

Balalakshmi, C.; Gopinath, K.; Govindarajan, M.; Lokesh, R.; Arumugam, A.; Alharbi, N.S.; Kadaikunnan, S.; Khaled, J.M. and Benelli, G. (2017): Green synthesis of gold nanoparticles using a cheap *Sphaeranthus indicus* extract: impact on plant cells and the aquatic crustacean *Artemia nauplii*. J. Photochem Photobiol B Biol., 173:598–605. https://doi.org/10.1016/j.jphotobiol.2017. 06.040

Bhushan, B. (2004): Handbook of Nanotechnology. Berlin-Heidelberg, Germany: Springer-Verlag. 10.1007/978-3-642-02525-9.

Campos,E. V. R.; Proença ,P. L. F.; Oliveira ,J. L.; Melville ,C. C; Vechia,J. F. D.; De Andrade,D., J., and Fraceto, L. F. (2018): Chitosan nanoparticles functionalized with β-cyclodextrin: a promising carrier for botanical pesticides. Scientific Reports . 8:2067 DOI:10.1038/ s41598-018-20602-y

Cheng, C.J.; Tietjen, G.T.; Saucier-Sawyer, J.K. and Saltzman, W.M.(2015): Nat Rev Drug Discov., 14:239-247. DOI:10.1038/nrd4503.

Clotuche, G.; Mailleux, A.; Fernandez, A.A.; Deneubourg, J.; Detrain, C. and Hance,T. (2011) : The formation of collective silk balls in the spider mite,*Tetranychus urticae* Koch. PLoS One., 6(4): e18854. doi:10.1371/journal.pone.0018854.

Clotuche, G.; Mailleux, A.C.; Yano, S.; Detrain,C.; Deneubourg, J.L. and Hance, T.(2013): Settlement decisions by the two-spotted spider mite *Tetranychus urticae*. Comptes Eendus Biologies, 336(2): 93-101. https://doi.org/10.1016/j.crvi.2013.02.006

Dittrich,V. (1962) : A comparative study of toxicological test methods on a population of the two-spotted spider mite,*T.urticae*. J. Econ. Entomol. , 55: 633-648.

El-Nour, K.M.M.A.; Eftaiha, A.; Al-Warthan, A. and Ammar, R.A.A. (2010): Synthesis and applications of silver nanoparticles. Arab. J. Chem., 3:135–140. doi: 10.1016/j.arabjc.2010.04.008.

Esumi, K.; Shiratori, M. ; Ishizuka, H.; Tano,T.; Torigoe, K. and Meguro, K. (1991): Preparation of bimetallic palladium-platinum colloids in organic solvent by solvent extraction-reduction. Langmuir,7(3):457-459. https://doi.org/10.1021/la00051a007.

Finney, D. J. (1971): Probit Analysis Cambridge University Press.

Fuchs, S.; Rende, E.; Crisanti, A. and Nolan, T. (2014): Disruption of aminergic signalling reveals novel compounds with distinct inhibitory effects on mosquito reproduction, locomotor function and survival. Sci. Reports, 4: (Article No. 5526). Doi:10.1038/srep05526.http://www.nature.com/srep/2014/140702 /srep05526/full/srep05526.html.

Govindarajan, M., and Benelli, G. (2016): One-pot green synthesis of silver nanocrystals using *Hymenodictyon orixense*: a cheap and effective tool against malaria, chikungunya and Japanese encephalitis mosquito vectors?. RSC Adv., 6:59021–59029.

Govindarajan, M.; Khater, H.F.; Panneerselvam, C. and Benelli, G. (2016a): One-pot biosynthesis of silver nanoparticles using *Nicandra physalodes*: a novel route for mosquito vector control with moderate toxicity on non-target water bugs. Res., Vet. Sci., 107:95–101.

Govindarajan, M.; Rajeswary, M.; Veerakumar, K.; Muthukumaran, U.; Hoti, S.L.; Khater, H.F. and Benelli, G. (2016b): Single-step biosynthesis and characterization of silver nanoparticles using *Zornia diphylla* leaves: a potent eco-friendly tool against malaria and arbovirus vectors. J. Photochem. Photobiol. B Biol., 161:482–489.

Jayaseelan, C.; Gandhi, P.R.; Rajasree, S.R.R.; Suman, T.Y. and Mary, R.R. (2018): Toxicity studies of nanofabricated palladium against filariasis and malaria vectors. Environ. Sci. Poll Res., 25:324–332.

Jinu, U.; Vaitheeswari, K.; Manish, T.; Benelli, G. and Venkatachalam, P. (2018): Nanotitania crystals induced efficient photocatalytic dye degradation, antimicrobial and larvicidal activity. J. Photochem. Photobiol. B Biol., 178:496–504.

Kaufman, R. and Sloley, D. (1996): Catabolism of dopamine and 5-hydroxytryptamine by monoamine oxidase in the ixodid tick, *Amblyomma herbraeum*. Insect Biochem Mol Biol., 26(1): 101-109

Kim,T.; Kobayashi, K. and Nagai, M. (2007): Preparation and characterization of platinum-ruthenium bimetallic nanoparticles using reverse microemulsions for fuel cell catalyst. Oleo Sci., 56(10):553-562.

Kirthi, A.V.; Rahuman, A.A.; Rajakumar, G.; Marimuthu, S.; Santhoshkumar, T.; Jayaseelan, C. and Velayutham, K. (2011): Acaricidal, pediculocidal and larvicidal activity of synthesized ZnO nanoparticles using wet chemical route against blood feeding parasites. Parasitol. Res., 109:461–472.

Lee, S.H. and Jun, B.H. (2019): Silver nanopartciles: Synthesis and application for nanomedicine. Int. J. Mol. Sci., 20:865. doi: 10.3390/ijms20040865.

Llorens, A.; Lloret, E.; Picouet, P.A.; Trbojevich, R. and Fernandez, A. (2012): Metallic-based micro and nanocomposites in food contact materials and active food packaging. Trends Food Sci. Technol., 24:19–29.

Medina, C.; Santos-Martinez, M. J.; Radomski, A.; Corrigan, O. I. and Radomski, M. W. (2007): Nanoparticles: pharmacological and toxicological significance. British J. Pharmacol., 150: 552–558.

Mittal, A.K.; Chisti, Y. and Banerjee, U.C. (2013): Synthesis of metallic nanoparticles using plant extract.Biotech.Adv., 31(2):346-356. DOI:

10.1016/j.biotechadv.2013.01.003.

Mizukoshi, Y.; Okitsu, K.; Maeda, Y.; Yamamoto, T.A.; Oshima, R. and Nagata, Y. (1997): Sonochemical preparation of bimetallic nanoparticles of gold/palladium in aqueous solution. J. Phys. Chem. B., 101(36): 7033-7037.

Mondal, S.; Roy, N.; Laskar, R.A. ; SK, I.; Basu, S.; Mandal, D. and Begum, N.A. (2011) : Biogenic synthesis of Ag,Au and bimetallic Au/Ag alloy nanoparticles using aqeous extract of mahogany (*Swietenia mahogani*) leaves. Colloid Surf. B. Biointerferences, 82(2):497-504.

Murugan, K.; Benelli, G.; Ayyappan, S.; Dinesh, D.; Panneerselvam, C.; Nicoletti, M.; Hwang, J.S.; Kumar, P.M.; Subramaniam, J., and Suresh, U. (2015a): Toxicity of seaweed-synthesized silver nanoparticles against the filariasis vector *Culex quinquefasciatus* and its impact on predation efficiency of the cyclopoid crustacean *Mesocyclops longisetus*. Parasitol. Res., 114(6): 2243–2253.

Murugan, K.; Benelli, G.; Panneerselvam, C.; Subramaniam, J.; Jeyalalitha, T.; Dinesh, D.; Nicoletti, M.; Hwang, J.S.; Suresh, U. and Madhiyazhagan, P. (2015b): *Cymbopogon citratus*-synthesized gold nanoparticles boost the predation efficiency of copepod *Mesocyclops aspericornis* against malaria and dengue mosquitoes. Exp. Parasitol., 153:129–138.

Murugan, K.; Dinesh, D.; Nataraj, D.; Subramaniam, J.; Amuthavalli, P.; Madhavan, J.; Rajasekar, A.; Rajan, M.; Thiruppathi, K.P.; Kumar, S.; Higuchi, A.; Nicoletti. M. and Benelli, G. (2018): Iron and iron oxide nanoparticles are highly toxic to *Culex quinquefasciatus* with little non-target effects on larvivorous fishes. Environ. Sci. Poll. Res., https://doi.org/10.1007/s11356-017-0313-7

Nakano, Y. and Asada, K. (1981): Hydrogen peroxide is scavenged by ascorbate-specific peroxidase in spinach chloroplasts. Plant Cell Physiol., 22:867-880.

Novaroli, L.; Reist, M.; Favre, E.; Carotti, A.; Catto, M. and Carrupt, P.A. (2005): Human recombinant monoamine oxidase B as reliable and efficient enzyme source for inhibitor screening. Bioorg. Med. Chem., 13(22): 6212-6217.

Oliveira, M.M.; Ugarte, D.; Zanchet, D. and Zarbina, A.J.G. (2005): Influence of synthetic parameters on the size, structure, and stability of dodecanethiol-stabilized silver nanoparticles. J. Colloid Interface Sci.,292:429–435. doi: 10.1016/j.jcis.2005.05.068.

Pillai, Z.S. and Kamat, P.V. (2004): What factors control the size and shape of silver nanoparticles in the citrate ion reduction method? J. Phys. Chem. B., 108:945–951. doi: 10.1021/jp037018r.

Rai, M.; Ribeiro, C.; Mattoso, L. and Duran, N. (2015): Nanotechnologies in Food and Agriculture. Heidelberg: Springer. P:347.

Rajaganesh, R.; Wei, H.; Syuhei, B.; Aziz, A.T.; Saleh, A.M.;

Devanesan, S.; Nicoletti, M. ; Canale, A. and Benelli, G. (2016): Carbon and silver nanoparticles in the fight against the filariasis vector *Culex quinquefasciatus*: genotoxicity and impact on behavioral traits of non-target aquatic organisms. Parasitol. Res., 115:1071–1083.

Rajakumar, G. and Rahuman, A.A. (2012): Acaricidal activity of aqueous extract and synthesized silver nanoparticles from *Manilkara zapota* against *Rhipicephalus (Boophilus) microplus*. Res. Vet. Sci., 93:303–309.

Rao, C.; Muller, A. and Cheetham, A.K. (2005): The Chemistry of Nanomaterials, Synthesis, Properties and Applications.Weinheim, Germany: Wiley-VCH.P: 761.

Sap-Iam, N.; Homklinchan, C.; Larpudomlert, R.; Warisnoicharoen, W.; Sereemaspun A. and Dubas, S. T. (2010): UV Irradiation-Induced silver nanoparticles as mosquito larvicides. J. Appl. Sci.,10: 3132-3136.

Schweizer, D. (2014): Transport of nanopesticides in saturated porous media. Masterarbeit, University of Vienna. Fakultät für Geowissenschaften, Geographie und Astronomie BetreuerIn: Hofmann, Thilo. URL: http://othes.univie.ac.at/34774/

Sedighi, A.; Imani,S.; Kashanian,G. R.; Najafi, H. and Fathipour,Y. (2019): Efficiency of Green Synthesized Silver Nanoparticles with Sweet Orange, *Citrus sinensis*(L.) (Rutaceae,Sapindales) against *Tribolium confusum* Duval. (Coleoptera, Tenebrionidae). J. Agr. Sci. Tech. , 21(6): 1485-1494.

Shankar,S.S. ; Rai, A.; Ahmad, A. and Sastry,M. (2004): Rapid synthesis of Au,Ag,and bimetallic Au core-Ag shell nanoparticles using Neem (*Azadirachta indica*) leaf broth. J. Colloid Interference Sci., 275(2):496-502.

Sharma, H.; Mishra ,P. K.; Talegaonkar ,S. and Vaidya ,B. (2015): Metal nanoparticles: a theranostic nanotool against cancer. Drug Discovery Today, 20(9):1143-1151. https://doi.org/10.1016/j. drudis.2015.05.009.

Teimouri, M.; Nejad, F.K.; Attar, F.; Saboury, A.A.; Kostova, I.; Benelli, G. and Falahati, F. (2018): Green fabricated gold nanoparticles: synthesis, characterization, degradation of 4-nitrophenol from industrial wastewater, and insecticidal activity—a review. J. Cleaner Prod., 184:740–753. https://doi.org/10.1016/j.jclepro.2018.02.268

Toppozada, A.; Abdallah,S. and Eldefrawi, M.E.(1966): Chemosterilization of larvae and adults of the egyptian cotton leafworm *Prodenia litura*, by apholate, metepa, and tepa. J.Econ. Entomol., 59: 1125-1128.https://academic.oup.com/jee/article-abstract/59/5/1125/2208549?redirectedFrom= fulltext